Polymerization Induced Epitaxy. Polyether Films on Graphite as Studied by Scanning Tunnelling Microscopy

Masahito Sano,* Darryl Y. Sasaki and Toyoki Kunitake

Molecular Architecture Project-JRDC, Kurume Research Park, Kurume, Fukuoka 830, Japan

Ultrathin, epitaxial films of polyethers are grown on the basal plane of graphite by conventional polymerization methods.

The formation of highly ordered macromolecules is of current interest in the field of material science. Ordered placement of linear polymers by epitaxial growth has formally been studied by crystallizing preformed polymer molecules on a solid surface from the solution or the melt under strictly controlled conditions.[1,2] Also, polymer crystals were epitaxially produced by topochemical solid-state polymerization of monomers.[3] Here, we report the first evidence of direct formation of ultrathin, epitaxial polymer films on a solid surface through conventional chemical synthetic methods.

In this preliminary report, we present the preparation of epitaxial polyether films on highly oriented pyrolytic graphite (HOPG) *via* ring-opening polymerization. The resulting polymeric films were identified by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), and their structures were probed by scanning tunnelling microscopy (STM). In order to ascertain that we are imaging polymeric films rather than some graphite artefacts, we have repeated the experiment using different initiators and monomers (cyclic ethers containing 2, 3, and 4 carbon atoms).

The cationic ring-opening reaction of polyethers is well documented.[4] Freshly cleaved HOPG was submerged in a solution of monomer followed by addition of an initiator. After 12 to 24 h, the reaction was quenched by ethanol. The HOPG was taken out and washed thoroughly with ethanol and with good solvents for the bulk polymer. For the preparation of poly(tetrahydrofuran) (PTHF), neat THF was polymerized at room temperature by either $(CF_3SO_2)_2O$, $BF_3{\cdot}OEt_2$, or $Et_3O^+(BF_4)^-$, producing the bulk polymers having the mass averaged molecular mass (M_r) of *ca.* 38 000 in all cases. Ethylene oxide (50 mol%) in CH_2Cl_2 with 5% $BF_3{\cdot}OEt_2$ and oxacyclobutane (50 mol%) in CH_2Cl_2 with 5% $Et_3O^+(BF_4)^-$ gave poly(ethylene oxide) (PEO, M_r = 800) and poly(oxacyclobutane) (POCB, M_r = 6 000), respectively, at −63 °C.

All the thus treated HOPG samples exhibited FTIR peaks at *ca.* 2950, 2870 and 1100 cm^{-1} and XPS indicated substantial increase of oxygen on the graphite surface after polymerization. The same XPS spectra showed no measurable quantities of initiator species of F, S and B and the subsequent STM images were reproducible regardless of the initiator. These observations established the presence of polyether films alone on the surface of HOPG. These polymeric films are not removed even by good solvents of the bulk polymers.

STM, operating in air at room temperature, revealed highly ordered, crystalline structures of each polyether extending over thousands of Ångstroms (Fig. 1). The long spacings between the bright spots are 12.3 Å for PTHF, 4.9 Å for POCB and 7.4 Å for PEO. The short spacing is measured to be 4.3 Å for all polymers. These STM images can be explained by assuming that the ether oxygen atom appears brighter than the alkanic carbon. It is well known that, on bare graphite, every other carbon atom is a predominant tunnelling site and appears brighter. Thus, we further assume that the adsorbate atom in the vicinity of the bright graphite carbon appears brighter than others that are away from it.[5]

Based on these assumptions, we present a model of epitaxial structures associated with the STM images in Fig. 2. The bright spots on the STM images are assigned to be the ether oxygen atoms that are located near the brighter graphite carbon atoms. A planar, all *trans* conformation places every other ether oxygen in the equivalent graphite carbon atoms and produces the spacings between these oxygens in complete agreement with the STM images. This model is also supported by the observation that POCB, although having a longer oxygen–oxygen distance than PEO, appears to have a shorter period in the STM image. The interchain short spacing of 4.3 Å is also in complete agreement with the distance between every other graphite hexagon. This orientation of the polymer is expected from the interaction of the hydrogen atoms of an aliphatic chain and the graphite hexagonal lattice.[6–8]

These planar, epitaxial structures are quite different from the bulk structures where POCB and PEO take helical forms.[9] Bulk POCB and PEO can assume planar zigzag forms only under special conditions such as inclusion of water molecules[10] or mechanical tension.[11] This communication is the first report of epitaxial structures of polyethers on a graphite surface. An STM study of PEO on HOPG by Yang and others[12] indicated that no epitaxial film was formed if the preformed polymer was cast from a solution. Therefore, we believe that the epitaxial orientation we observed has occurred during the course of the polymerization process in the vicinity of the

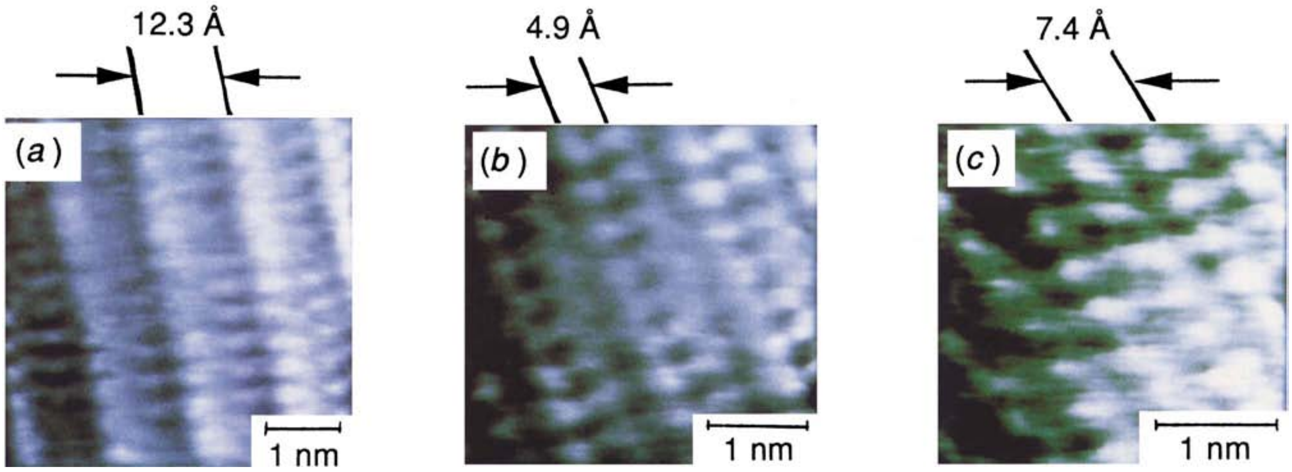

Fig. 1 Variable current STM images of (*a*) PTHF, (*b*) POCB and (*c*) PEO, taken at 200 pA with a bias of 1.0 V

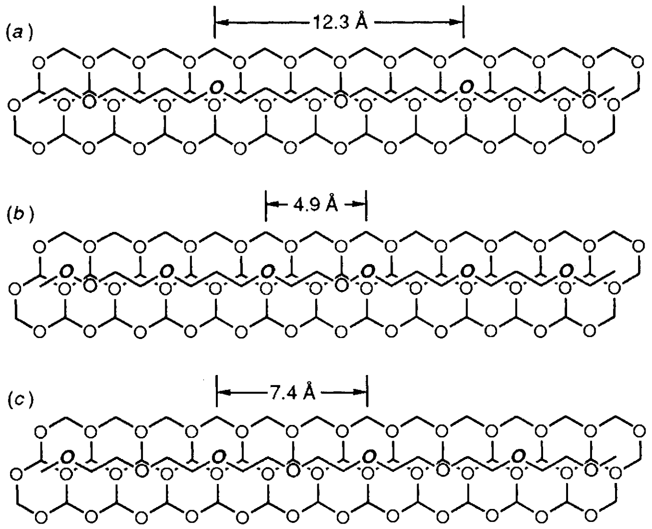

Fig. 2 Models of epitaxial structures that explain the contrast in the STM images for (*a*) PTHF, (*b*) POCB and (*c*) PEO in Fig. 1. A small circle in the honeycomb represents a bright spot on the STM graphite image. Lying flat on the graphite is a polymer molecule with a thick zigzag line denoting an alkanic chain. The oxygen atom shown in the bold, italic character lies in the neighbourhood of the bright graphite point and appears differently from the other oxygen atoms.

surface rather than as a result of the surface crystallization of polymeric chains first formed in the bulk solution.

Lastly, these images are not unique to each polymer. The same sample can yield various other images, one example of which is shown in Fig. 3 for PTHF. Unlike the images of Fig. 1 where every bright spot has uniform contrast, this image shows the modulations of contrast along and perpendicular to the lines of bright spots. A detailed analysis of these images, including moiré patterns which illustrate how the polymer chain is oriented with respect to the graphite lattice, will be reported elsewhere. This new technique will allow us to control molecular orientation in two dimensions and to investigate polymer physics and chemistry on surfaces at the nanometer level.

Received, 14th May 1992; Com. 2/02524H

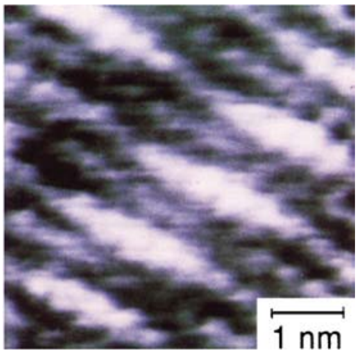

Fig. 3 A different STM image of PTHF taken from the same sample as shown in Fig. 1. A variation of contrast along the bright lines is due to a moiré pattern which can be identified easily in a wide scan image (not shown here).

References

1 K. A. Mauritz, E. Baer and A. J. Hopfinger, *J. Polym. Sci. Macromol. Rev.*, 1978, **13**, 1.
2 J. C. Wittmann and B. Lotz, *Prog. Polym. Sci.*, 1990, **15**, 909.
3 G. S. Swei, J. B. Lando, S. E. Rickert and K. A. Mauritz, in *Encyclopedia of Polymer Science and Technology*, ed. J. I. Kroschwitz, Wiley, New York, 1986, vol. 6, pp. 209–225.
4 See for instance, G. Odian, *Principles of Polymerization*, Wiley-Interscience, New York, 2nd edn., 1981.
5 G. C. McGonigal, R. H. Bernhardt and D. J. Thomson, *Appl. Phys. Lett.*, 1990, **57**, 28.
6 J. P. Rabe and S. Buchholz, *Science*, 1991, **253**, 424.
7 A. J. Groszek, *Proc. R. Soc. London Ser. A*, 1970, **314**, 473.
8 P. R. Baukema and A. J. Hopfinger, *J. Polym. Sci. Polym. Phys. Ed.*, 1982, **20**, 399.
9 H. Tadokoro, *J. Polym. Sci. C*, 1966, **15**, 1.
10 H. Kakida, D. Makino, Y. Chatani, M. Kobayashi and H. Tadokoro, *Macromolecules*, 1970, **3**, 569.
11 Y. Takahashi, I. Sumita and H. Tadokoro, *J. Polym. Phys. Ed.*, 1973, **11**, 2113.
12 R. Yang, X. R. Yang, D. F. Evans, W. A. Hendrickson and J. Baker, *J. Phys. Chem*, 1990, **94**, 6123.